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UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

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Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of Jan. 09, 2005 to Feb. 09, 2005, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CuInSe₂-based Solar Cells).

Task 2: CuInSe₂-based Solar Cells

In Line Evaporation System

During the present time period, the effort of developing roll-to-roll Cu(InGa)Se₂ deposition on polymer web was concentrated on system upgrades and modifications to increase deposition rate and to incorporate Na into the Cu(InGa)Se₂ film.

In a first step, the insulation of the copper Cu has been modified to accommodate higher temperatures. Multilayer graphelt/Ta/grafoil parts have been replaced with rigid alumina and Ta foils. The main reason for this change was to have a rigid insulation system that would be reproducible and would have predictable thermal characteristics. Other graphite parts in the source were also changed and replaced with boron nitride so as to eliminate the reaction with alumina insulation. Presently the only graphite part left in the source is the heater.

A new Se source was found to be necessary because the old design was found to be leaking as the temperature was increased. As a result, the Se was effusing not only

through the manifold; but also through the grafoil seal, between the cap and the body of the source.

As far as the Na source is concerned, the decision was made to use the design of the present metal sources. This would be the most expedient approach, since there would be no need for design and testing of a new source. Furthermore, the Na source control component has already been added to the present software program running the system. The Na source will be heated by a DC power supply that will provide additional system monitoring capability.

Wide Bandgap Materials

Cu(InAl)Se₂

Cu(InAl)Se₂ films have been deposited using a 3-stage evaporation process incorporating end-point detection of the substrate temperature (T_{ss}) to control the final composition. A description of the process and characterization of the films follows. Figure 1 shows the time-temperature profile of the elemental sources and the substrate heater power during a typical deposition. Figure 2 shows the measured T_{ss} profile during a typical deposition. The 3-stage process is characterized by sequential deposition and reaction of 3 layers. In the first stage, In, Al, and Se are deposited on the Mo coated soda-lime glass at relatively low T_{ss} . Subsequently, Cu and Se are deposited onto the film to form the chalcopyrite phase at higher T_{ss} and then continued to form a Cu-Se phase on the film surface. Finally, In, Al, and Se are deposited to make the film slightly Cu poor, so it is suitable for devices. The typical final composition gives $[Cu]/[In+Al] = 0.8-0.9$. Figure 2 shows that at time A during the second stage a sudden drop in T_{ss} can be measured. This corresponds to the formation of the Cu-Se phase on the film, which changes the emissivity. T_{ss} later increases when the Cu-Se phase is consumed in the third stage. The reproducibility of the 3-stage process owes to the temperature drop at time A since it enables the operator to carefully monitor the subsequent film growth.

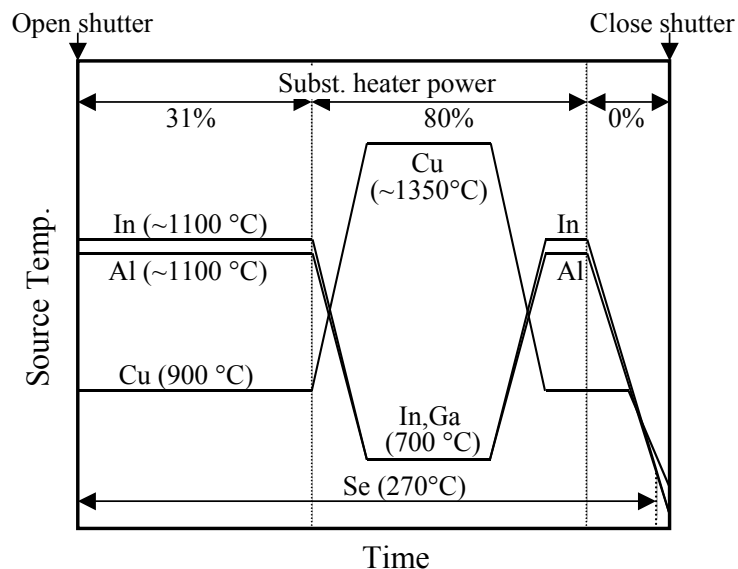


Figure 1. Source temperatures and substrate heater power during the deposition.

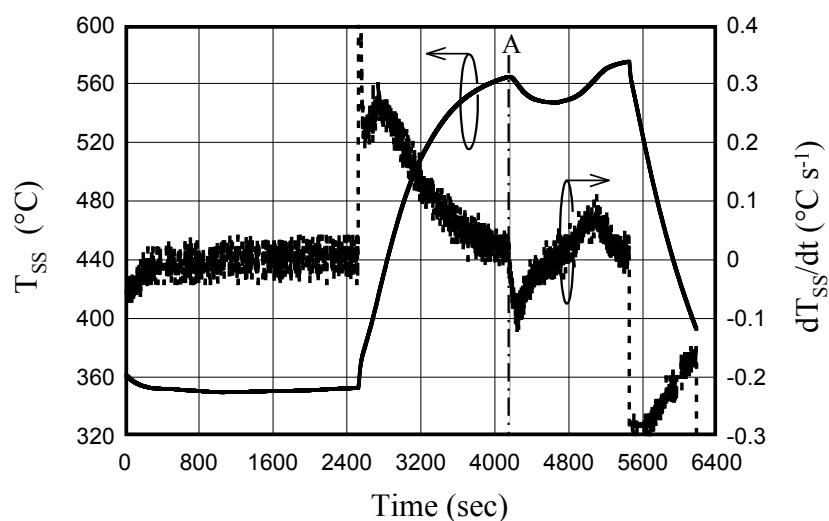


Figure 2. Typical substrate temperature profile and its first derivative.

Films were grown with different relative Al contents and the (112) XRD peaks are shown in Figure 3. Clear shifts to high angle and broadening of the peak with increasing Al content ($[Al]/[In+Al]$) can be seen. In Figure 4, the surface morphology of low ($[Al]/[In+Al]=0.17$) and high ($[Al]/[In+Al]=0.58$) Al content films are shown by SEM micrographs. The low Al film contains 1-2 μm grains, while the high Al film has submicron grains.

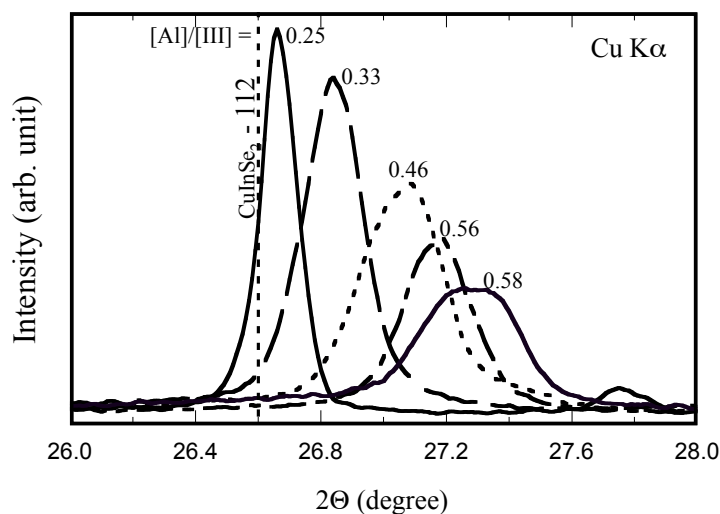


Figure 3. 112 XRD peaks from films with various Al content.

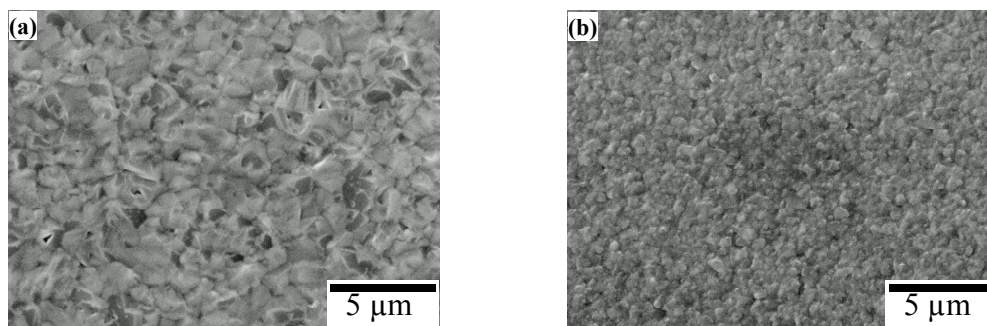


Figure 4. Surface morphologies of (a) low Al ($[Al]/[In+Al]=0.17$) and (b) high Al ($[Al]/[In+Al]=0.58$) content films.

Solar cells were fabricated using the standard device structure with CdS/ZnO/ITO window layers. Figure 5 shows J-V curves of the best solar cells with different Al content. Devices with $[Al]/[In+Al] \sim 0.2$ show a reproducible efficiency $> 12\%$. So far, the best performance obtained is an efficiency of 13.6% , with $V_{OC} = 0.546V$, $J_{SC} = 32.8 \text{ mA cm}^{-2}$, $FF = 75.9\%$ so no improvement with the 3-stage process has been achieved. As previously reported, higher $[Al]/[In+Al]$ samples generally peel off during CdS buffer layer deposition. The exception is with stoichiometric or Cu-rich films with $[Cu]/[In+Al] \geq 1.0$ which have better adhesion. Devices in this case, as with $[Al]/[In+Al] = 0.52$ in Figure 5, are fabricated after a KCN etch.

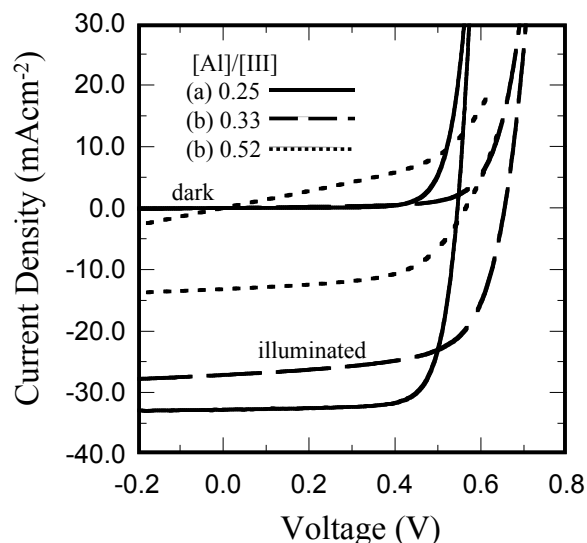


Figure 5. J-V curves with (a) $[\text{Al}]/[\text{In}+\text{Al}]=0.25$, (b) $[\text{Al}]/[\text{In}+\text{Al}]=0.33$, and (c) $[\text{Al}]/[\text{In}+\text{Al}]=0.52$.

Cu(InGa)(SeS)₂ Formation by H₂Se/H₂S Reaction

Efforts to characterize the formation of Cu(InGa)(SeS)₂ by reaction of Cu-Ga-In precursor layers in H₂Se/H₂S are proceeding after a renovation and safety upgrade of the hazardous gas laboratories at IEC were completed. The objective of this work is to determine the effects of time-temperature-concentration profiles to enable independent control of Ga and S through-film composition and higher V_{OC} in devices made with the reacted films.

Two different processes are being used to sputter the precursor layers. In one case, separate Cu/Ga/In layers are sequentially deposited from 3 elemental sputter targets. This allows independent control of Cu/(In+Ga) and Ga/(In+Ga). In the second case, a Cu_{0.8}Ga_{0.2} alloy target is used and followed by an elemental In layer. In this case the Cu/(In+Ga) and Ga/(In+Ga) ratios are coupled. Precursors were deposited with Cu/(In+Ga) = 0.9 which gives Ga/(In+Ga) = 0.225. SEM micrographs of the 2 types of precursors are shown in Figure 6.

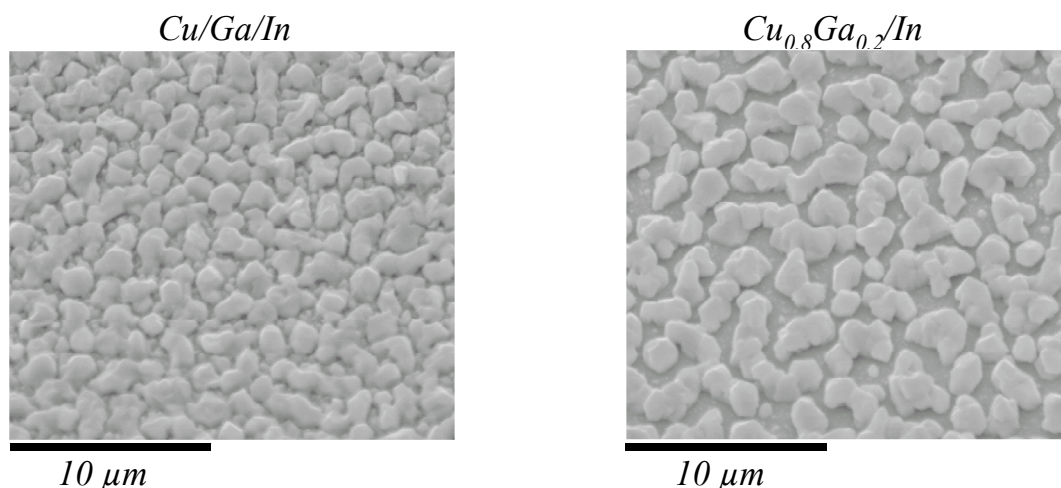


Figure 6. SEM micrographs of sputtered Cu/Ga/In and Cu_{0.8}Ga_{0.2}/In precursors.

Fundamental Materials and Interface Characterization

CdS deposition

We have previously compared Cu(InGa)Se₂ devices with CdS deposited by standard chemical bath deposition (CBD) and high utilization chemical surface deposition (CSD) and found similar performance but with evidence of slightly higher V_{OC} using the CBD process. To further determine whether there is any difference in devices, a more extensive set of samples was processed. A total of 10 Cu(InGa)Se₂ samples from 2 different, but nominally identical runs, were processed using 5 with each CdS process. This gave a total of 30 devices with each type. Results are summarized in Table 1, which lists the best device of each type and the average and standard deviation. While the best cell with CBD CdS was slightly better, the averages were the same indicating no difference in device performance. The variability in device performance which yields 12.9% overall average efficiency compared to 14.8 – 15.4 % for the best cells is due to variation in the shunt conductance. Causes for this are being investigated.

Table 1. Comparison of Cu(InGa)Se₂ devices with CBD and CdS emitter layers based on 30 devices of each type.

CdS dep.		Eff (%)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF (%)	R _{OC} (Ω-cm ²)	G _{SC} (mS/cm ²)
CBD	Best cell	15.4	0.633	31.7	76.6	1.4	1
	Average	12.9	0.604	30.6	69.0	2.2	5
	Std. Dev.	1.7	0.019	0.8	8.7	1.0	8
CSD	Best cell	14.8	0.621	31.4	76.0	1.4	2
	Average	12.8	0.605	30.6	68.8	1.9	4
	Std. Dev.	1.2	0.013	0.5	5.1	0.4	2

Optical Characterization

Spectroscopic ellipsometry is being used to characterize the optical constants of CdS layers, to determine if the CdS properties are affected by the Cu(InGa)Se₂ surface or with different CdS deposition processes. For characterization of films deposited on Cu(InGa)Se₂, a smooth surface must be used. This is formed by a smoothing Br-etch followed by a KCN etch to remove excess Se on the surface, as shown in a previous report.

The refractive index (n) and extinction coefficient (k) of CdS films formed by CBD on Mo and on smoothed Cu(InGa)Se₂ are compared in Figure 7. Prior to CdS deposition, the precise optical constants of the Mo and Cu(InGa)Se₂ were determined. The optical model used to determine the n and k of the CdS includes the bulk Mo or Cu(InGa)Se₂, then a thin interface/roughness layer fit using an effective medium approximation (EMA), then the bulk CdS film, and finally, a surface roughness EMA layer. A harmonic oscillator model is used for the CdS layer. The CdS films were ~ 50 nm thick. The results in Figure 7 are also compared to n and k, for a thicker CdS film deposited on crystallized ITO in a CdTe device; that was characterized after the CdTe was peeled off. In this case, the CdS was annealed in the presence of CdCl₂ during device processing. The CdS on Mo or Cu(InGa)Se₂ has a much broader fundamental transition at 2.4 eV, while the CdS in the CdTe more closely matches published properties of crystalline CdS. These differ also in the high-energy range > 3.5 eV. The reasons for these differences in optical behavior are being further investigated. Possible reasons include: different crystallinity of the annealed CdS in the CdTe device, differences in the CdS/Cu(InGa)Se₂ and CdS/Mo interfaces, and thickness effects in the CdS or in the optical fitting.

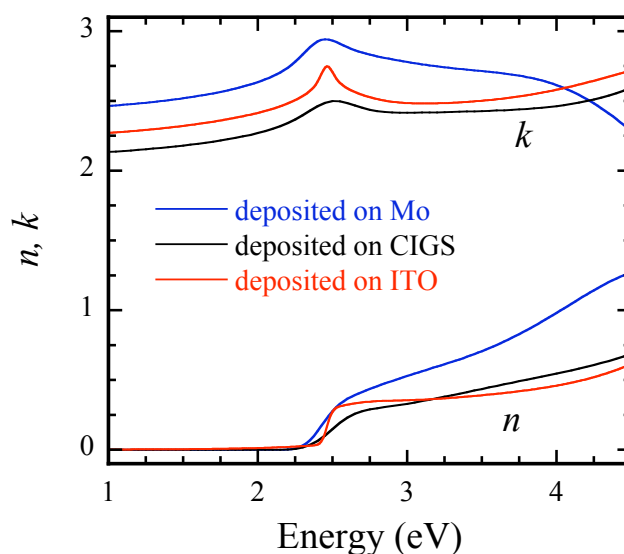


Figure 7. Optical constants of CBD CdS layers deposited on different substrates. The layer on ITO was annealed during CdTe device processing.

Collaboration

Energy Photovoltaics

IEC has collaborated with EPV on alternative back contacts. In particular, IEC has fabricated and characterized devices using alternative back contacts deposited by EPV, which, should provide improved reflectivity for devices with thin Cu(InGa)Se₂ absorbers. In addition, IEC has collaborated with EPV on evaporation source design and provided a design for a laboratory scale Cu evaporation source.

Best regards,

Robert W. Birkmire
Director

RWB/bj

Cc: Gerri Hobbs, UD Research Office
Carolyn Lopez, NREL
Paula Newton
Erten Eser
William N. Shafarman

